

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-035675

(43)Date of publication of application : 09.02.1999

(51)Int.Cl.

C08G 67/00
C08F 8/00
C08G 18/83
C08G 63/91
C08G 64/42
C08G 65/48
C08G 69/48
C08G 77/38

(21)Application number : 09-209847

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(22)Date of filing : 18.07.1997

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(54) REVERSIBLY THERMALLY CLEAVABLE RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a thermally cleavable resin having a crosslinked structure and high physical properties at the ordinary temperature but capable of being thermally cleaved to produce a resin low in melting viscosity and excellent in moldability by subjecting an alkenyl ether group-containing compound and a carboxyl group-containing compound to an addition reaction in the presence of a specific catalyst.

SOLUTION: This reversibly thermally cleavable resin composition is obtained by subjecting (A) a compound containing (m) alkenyl ether groups and (B) a compound containing (n) carboxyl groups to an addition reaction in the presence of a catalyst comprising a phenolic compound (preferably nitrophenol, etc.), or a hydroxyamine (preferably ethanolamine, etc.), [(m), (n) are each ≥ 2 , wherein at least one of (m), (n) is 3 or larger]. The component A includes triethylene glycol dipropenyl ether and a copolymer of a propenyl ether-containing acrylic monomer with styrene monomer. The component B includes dodecanedicarboxylic acid and acrylic acid copolymers.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of

rejection]

[Kind of final disposal of application other than
the examiner's decision of rejection or
application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's
decision of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

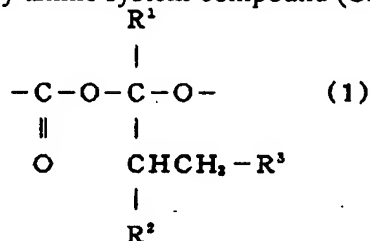
[Claim 1] Heat cleavage nature resin characterized by carrying out the addition reaction of the compound (A) which contains m alkenyl ether groups in intramolecular, and the compound (B) which contains n carboxyl groups in intramolecular under existence of the catalyst which consists of a phenol system compound (C1) or a hydroxy amine (C2), and being obtained (however, m and n are two or more integers, and at least one of m and the n is three or more integers.)

[Claim 2] Heat cleavage nature resin containing one or more sorts of organic radicals (a) chosen from the group which this compound (A) becomes from the radical of the heterocycle structure which contains a hydrocarbon group, a ether group, a thioether radical, a carbonyl group, an ester group, an imino group, an amide group, an imide radical, a urethane group, an urea radical, a carbonate radical, a siloxy radical and a nitrogen atom, or an oxygen atom in the chain according to claim 1.

[Claim 3] Heat cleavage nature resin containing one or more sorts of organic radicals (b) chosen from the group which this compound (B) becomes from the radical of the heterocycle structure which contains a hydrocarbon group, a ether group, a thioether radical, a carbonyl group, an ester group, an imino group, an amide group, an imide radical, a urethane group, an urea radical, a carbonate radical, a siloxy radical and a nitrogen atom, or an oxygen atom in the chain according to claim 1 or 2.

[Claim 4] Claims 1-3 these whose alkenyl ether groups are a propenyl ether group or a vinyl ether radical are heat cleavage nature resin of a publication either.

[Claim 5] The heat cleavage nature resin constituent characterized by consisting of a catalyst of the resin (D) which has the divalent chemical bond expressed with the following general formula (1) in a chain and a phenol system compound (C1), or a hydroxy amine system compound (C2).



(In R1, a hydrogen atom or methyl group; R2, and R3 express a hydrogen atom or the alkyl group of carbon numbers 1-3 among a formula)

[Claim 6] The heat cleavage nature resin constituent according to claim 5 which are one or more sorts of resin chosen from the group which this resin (D) becomes from polystyrene system resin, acrylic resin, polyolefine system resin, polyether system resin, polysiloxane system resin, polycarbonate system resin, polyester system resin, polyamide system resin, and polyurethane system resin.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to reversible heat cleavage nature resin. In more detail, in ordinary temperature, since it has the structure of cross linkage, in spite of being quantity physical properties, in order that the chemical bond of the structure of cross linkage may cleave with heating, it is related with the heat cleavage nature resin constituent which became low melt viscosity and was excellent in the moldability.

[0002]

[Description of the Prior Art] Since conventional thermoplastics, such as polypropylene, polyethylene, and polystyrene, does not have the structure of cross linkage, it is common for a physical-properties side to be inadequate. If the structure of cross linkage is introduced into these thermoplastics, physical properties will improve, but since heat deflection temperature rises, thermoforming becomes difficult. Although ionomer resin is conventionally known as thermoplastics with the structure of cross linkage, there is no thing high [this] thermoforming temperature and satisfying as thermoplastics with the structure of cross linkage now.

[0003]

[Problem(s) to be Solved by the Invention] The technical problem which this invention tends to solve is by heating the structure of cross linkage, though it is holdings physical properties to offer the thermoplastics with which the specific chemical bond of the structure of cross linkage cleft and with which melt viscosity was excellent in the low moldability.

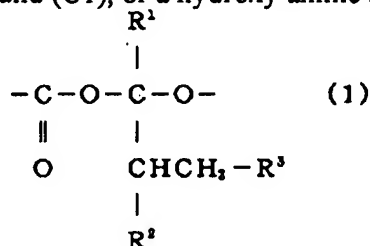
[0004]

[Means for Solving the Problem] As a result of examining wholeheartedly the catalyst suitable for the chemical bond and this which cause an addition reaction and a cleavage reaction reversibly, this invention persons found out the specific catalyst which can control reversibly thermoplastics and an addition reaction with the structure of cross linkage, and a cleavage reaction as resin with a sufficient moldability, though it was high physical properties, and reached this invention.

[0005] Namely, the compound with which the 1st invention contains m alkenyl ether groups in intramolecular (A), The compound (B) which contains n carboxyl groups in intramolecular under the catalyst existence of a phenol system compound (C1) or a hydroxy-amine system compound (C2) It is heat cleavage nature resin (I) (however, m and n are two or more integers, and either m or n are three or more integers at least) which is made to carry out an addition reaction and is obtained.

[0006] Moreover, the 2nd invention is a heat cleavage nature resin constituent (II) characterized by consisting of a catalyst of the resin (D) which has the divalent chemical

bond expressed with the following general formula (1) in a chain and a phenol system compound (C1), or a hydroxy amine system compound (C2).



(In R¹, a hydrogen atom or methyl group; R², and R³ express a hydrogen atom or the alkyl group of carbon numbers 1-3 among a formula)

[0007]

[The gestalt of invention implementation] A low molecular weight compound is sufficient as the compound (A) which contains the alkenyl ether group in the 1st invention among this inventions, and a high molecular compound or a prepolymer is sufficient as it. Moreover, an alkenyl ether group may be in any in the side chain of a molecule among the end of a compound, and a chain. A carbon number is usually the alkenyl ether group of 2-6, as for the alkenyl ether group of this invention, a propenyl ether group, a vinyl ether radical, an isopropenyl ether radical, etc. are specifically mentioned, and desirable things are a propenyl ether group and a vinyl ether radical. Furthermore, a compound (A) may also contain organic radicals (a), such as a radical of the heterocycle structure which contains a hydrocarbon group, a ether group, a thioether radical, a carbonyl group, an ester group, an imino group, an amide group, a urethane group, an urea radical, a carbonate radical, a siloxy radical, a nitrogen atom, or an oxygen atom in the chain.

[0008] In the case of a low molecular weight compound, as an example of a compound (A), vinyl ether radical content compounds [, such as propenyl ether group content compound; triethylene glycol divinyl ether,], such as for example, the triethylene glycol dipropenyl ether and the ethylene glycol dipropenyl ether, etc. are mentioned. The copolymer of the acrylic monomer and styrene monomer in which for example, a propenyl ether group is included in the case of a high molecular compound; the acrylic copolymer of the monomer and the acrylic monomer containing a vinyl ether radical etc. is mentioned.

[0009] Furthermore, a low molecular weight compound is sufficient as the compound (A) which contains the carboxyl group in the 1st invention among this inventions, and a high molecular compound or a prepolymer is sufficient as it. Moreover, a carboxyl group may be in any in the side chain of a molecule among the end of a compound, and a chain. Furthermore, a compound (B) may also contain the organic radical (a) mentioned above in (A), and the same organic radical (b) in the chain.

[0010] As an example of a compound (B), aromatic polycarboxylic acids, such as the Pori fatty acids, such as the case of a low molecular weight compound, for example, dodecane diacid etc., and a terephthalic acid, etc. are mentioned. The case of a high molecular compound, for example, the styrene copolymer containing an acrylic-acid copolymer; carboxyl group,, a carboxyl group end or the polyester of a side chain, a polyamide, polyurethane, etc. are mentioned.

[0011] The values of m in this invention and n are two or more integers, respectively, and at least one of m and the n is three or more integers.

[0012] As a catalyst (C) which can control the reversibility of the addition reaction and cleavage reaction in this invention, a phenol system compound (C1) and a hydroxy amine system compound (C2) are mentioned.

[0013] As a phenol system compound (C1) in this invention A phenol, a nitrophenol, a dinitrophenol, a trinitrophenol, A BUROMO phenol, fluorophenol, chlorophenol, an iodine phenol, An aminophenol, a monoalkyl phenol, a dialkyl phenol, Univalent phenols, such as a trialkyl phenol, tetra-alkylphenol, and PENTA alkylphenol; A catechol, Polyhydric phenols, such as resorcinol, hydroquinone, and pyrogallol; a naphthol etc. is mentioned and things desirable [among these] are a nitrophenol, a phenol, and chlorophenol.

[0014] Moreover, as a hydroxy amine system compound (C2), the alkanolamines of mono-alkanolamine, dialkanolamine, and a thoria RUKANORU amine are mentioned, and things desirable [among these] are triethanolamine, diethanolamine, and ethanolamine.

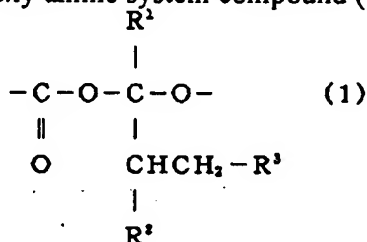
[0015] although especially the amount of the catalyst used is not limited -- an alkenyl ether group -- receiving -- usually -- 1-50-mol % -- it is 30-40-mol % preferably.

[0016] A compound (A), and (B) and a catalyst (C) are mixed and heated as a process of the heat cleavage nature resin of this invention, and the addition reaction of an alkenyl ether group and a carboxyl group is performed. (A) Or when (B) is a solid, it may mix in the state of powder, and you may use, and it may be made to dissolve in an organic solvent and you may use.

[0017] Although the temperature of the addition reaction of the alkenyl ether group and carboxyl group in the heat cleavage nature resin (I) of this invention changes with classes of catalyst (C), it is usually 100 degrees C - 140 degrees C. For example, when a nitrophenol is used as a catalyst, an addition reaction is completed within 1 hour at 100 degrees C.

[0018] Although the temperature of the heat cleavage reaction of a chemical bond expressed with the below-mentioned general formula (1) in the thermoplastics (I) of this invention changes with classes of catalyst, it is usually 130 degrees C - 160 degrees C. For example, when a nitrophenol is used as a catalyst, a heat cleavage reaction is completed within 1 hour at 130 degrees C.

[0019] The 2nd invention is a heat cleavage nature resin constituent (II) characterized by consisting of a catalyst of the resin (D) which has the divalent chemical bond expressed with the following general formula (1) in a chain and a phenol system compound (C1), or a hydroxy amine system compound (C2) among this inventions.



(In R1, a hydrogen atom or methyl group; R2, and R3 express a hydrogen atom or the

alkyl group of carbon numbers 1-3 among a formula.)

[0020] Although especially the class of resin (D) which has a chemical bond of the heat cleavage nature resin constituents (II) of this invention is not limited, it may be resin which was stated by explanation of the 1st invention and which is obtained by the addition reaction of the compound (A) which contains an alkenyl ether group in intramolecular, and the compound (B) which contains a carboxyl group in intramolecular, and a high molecular compound or a prepolymer is [a low molecular weight compound is sufficient as a compound (A) and (B), and] sufficient as them. Acrylic resin, polystyrene system resin, polyolefine system resin, polyurethane system resin, polyester system resin, polyamide system resin, polyether system resin, polysiloxane system resin, polycarbonate system resin, etc. can be used for the class of (A) or (B) which is a high molecular compound, and they are acrylic resin, polystyrene system resin, polyolefine system resin, polyurethane system resin, polyester system resin, and polyamide system resin preferably. Acrylic resin, polystyrene system resin, and polyolefine system resin are obtained by carrying out copolymerization of the acrylic monomer which contains an alkenyl ether group, for example to a copolymerizable vinyl system monomer as an approach of introducing an alkenyl ether group into the frame of resin. Moreover, as an approach of introducing a carboxyl group into the frame of resin, by carrying out copolymerization of the acrylic-acid monomer to a copolymerizable vinyl system monomer, acrylic resin, polystyrene system resin, and polyolefine system resin are obtained, and polycarboxylic acid is superfluous and there are an approach of obtaining polyester system resin and polyamide system resin, the polyol which has a carboxyl group further, the method of obtaining polyurethane resin from the poly isocyanate, etc.

[0021] The same phenol system compound (C1) as what is used by the 1st invention, and a hydroxy amine system compound (C2) can be used for the catalyst used as a heat cleavage reaction.

[0022] Although the temperature of the cleavage reaction of the heat cleavage nature resin (II) of this invention changes with classes of catalyst, it is usually 130 degrees C - 160 degrees C. For example, when a nitrophenol catalyst is used, a cleavage reaction is completed within 1 hour at 130 degrees C.

[0023] Since the catalyst of a phenol system compound (C1) and a hydroxy amine system compound (C2) exists, the heat cleavage nature resin (I) of the 1st invention and the heat cleavage nature resin (II) of the 2nd invention have the features that the chemical bond shown by the above-mentioned general formula (1) cleaves with heating, molecular weight becomes low unlike the time of being the macromolecule of the structure of cross linkage of ordinary temperature, and the melt viscosity of resin becomes remarkably low. Therefore, it excels in the moldability in the case of fabrication, such as casting, extrusion molding, compression molding, transfer molding, injection molding, and intake shaping.

[0024] In addition, although a cleavage reaction occurs even if other catalysts, for example, a 2-ethylhexyl phosphoric acid, are used for the chemical bond expressed with the above-mentioned general formula (1), there is a fault that the dissociated propenyl ether group will cause self-polymerization immediately. When the phenol system compound (C1) and hydroxy amine system compound (C2) which are used by this invention are used as a catalyst to it, there is such no evil and hypoviscosity-ization at the time of melting can be reversibly realized as a stable resin constituent.

[0025]

[Example] Hereafter, although an example explains this invention further, this invention is not limited to this. The "section" expresses the weight section below.

[0026] the <manufacture of resin> example 1 -- first, the phenothiazin 5 section was made to react at 100 degrees C for 5 hours as the methacrylic-acid-2-hydroxyethyl 100 section, the glycidyl propenyl 100 section, the triethylamine 10 section, and polymerization inhibitor, and the propenyl ether group content acrylate monomer was obtained after distillation purification. Next, by making this propenyl ether group content acrylate monomer 52 section and the styrene monomer 48 section into a polymerization initiator, the azo-isobutyro-dinitrile (azobisisobutironitoru) 3 section and the dodecane thiol 0.1 section were dissolved in the xylene 100 section, the polymerization reaction was carried out at 100 degrees C for 4 hours, and the xylene solution of a propenyl ether group content styrene system copolymer (the propenyl ether of intramolecular number average molecular weight 5000, base 15) was obtained. The dodecane diacid 10 section and the nitrophenol 4 section were added to this propenyl ether group content styrene copolymer solution, the addition reaction was carried out at 100 degrees C, and the heat cleavage nature resin of this invention was obtained after reduced pressure drying.

[0027] the example 1 of a comparison -- the demethanol was first performed for the phenothiazin 5 section under reduced pressure at 80 degrees C as the methacrylic-acid-2-hydroxyethyl 100 section, the sodium methylate 100 section, and polymerization inhibitor. After adding the epichlorohydrin 100 section to it and making it react at 80 degrees C for 4 hours, rinsing removed the salt which deposited and the glycidyl ether radical content acrylate monomer was obtained. Next, the azobisisobutironitoru3 section and the dodecane thiol 0.1 section were dissolved in the xylene 100 section, the polymerization reaction of this glycidyl ether radical content acrylate monomer 40 section and the styrene monomer 60 section was carried out at 100 degrees C for 4 hours, and the xylene solution of a glycidyl ether radical content styrene system copolymer (the propenyl ether of intramolecular number average molecular weight 7000, base 15) was obtained. This glycidyl ether radical content styrene polymer 100 section and the dodecane diacid 10 section were made to react at 150 degrees C, and comparative heat-curing mold resin was obtained.

[0028] In the example of comparison 2 example 1, comparative resin was similarly obtained except using the 2-ethylhexyl phosphoric-acid 4 section instead of a nitrophenol as a catalyst. In addition, when temperature was raised and this resin was heated from 100 degrees C to 140 more degrees C, the propenyl ether group carried out self-polymerization for the phosphoric ester system catalyst, and it became thermosetting resin, and thermofusion was not carried out even if heated.

[0029] (The approach by JISK7202) estimated <evaluation of resin> each resin in a melt flow rate (approach by JISK7210), and the Rockwell hardness. In addition, the melt flow rate (MFR) was measured at a 2.16 kgf/mm load and the temperature of 230 degrees C. Moreover, polypropylene (grand polymer company make, product name J605) was used as a criterion of thermoplastics. An evaluation result is shown in Table 1.

[0030]

[Table 1]

	MFR	硬さ
	g/10分	HRM
実施例 1	12.3	98
比較例 1	0	102
比較例 2	0	98
ポリプロピレン	9.0	76

[0031] The heat cleavage nature resin of this invention showed the MFR value more than the polypropylene which is typical thermoplastics. Since the catalyst from which this invention differs was used, as for the example 2 of a comparison, a fluidity was not shown in 230 degrees C. Moreover, it is admitted that the heat cleavage nature resin of this invention has a degree of hardness equivalent to the epoxy system thermosetting resin of the example 1 of a comparison in respect of hardness.

[Effect of the Invention]

[0032] Although the heat cleavage nature resin of this invention introduces into intramolecular the chemical bond which causes a reversible addition cleavage reaction as the structure of cross linkage and a heat cleavage reaction is enabled, having the high physical properties of the resin of a bridge formation mold and the moldability which was excellent in the resin of the mold non-constructing a bridge is admitted by using the specific catalyst which does not cause self-polymerization as side reaction. With conventional thermoplastics, the mold goods of high physical properties which were not obtained will be obtained, having a moldability equivalent to conventional thermoplastics, since the heat cleavage nature resin of this invention has the low viscosity at the time of thermofusion. Moreover, since heat cleavage nature is shown unlike conventional bridge formation mold resin, it is resin excellent also in recycle nature. As an example of mold goods with the suitable resin constituent of this invention, fiber, knitting, a nonwoven fabric, a network, a rope, a film, a sheet, a plate, a rod, various containers, a tube, various components, and various kinds of other mold goods are raised.

[Translation done.]